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PATENT SPECIFICATION

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(19)

(72) Inventor MATTHIAS COEMEN

(54) GLASS COMPOSITION

(71) We, CARL-ZEISS-STIFTUNG, a Foundation established under the Laws of Germany, trading as JENAER GLASWERK SCHOTT & GEN., of 10 Hattenbergstrasse, 65, Mainz, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to glass compositions and is concerned with glass which, in the form of fibres, is suitable as a reinforcement for cement, mortar and concrete or which, in the form of hollow spheres or in aerated form, is suitable for incorporation in light concrete.

It is known that the resistance of cement, mortar and concrete to stress, impact and abrasion can be considerably increased by the addition of glass fibres. The use of hollow glass spheres or glass in aerated form, i.e. aero glass, as an aggregate in light concrete has the advantage of increasing the resistance to pressure and of an absence of water absorption as compared with polystyrene or other aerated plastics. In Portland cement, however, fibres or hollow spheres of the usual types of glass are rapidly corroded because of the high pH, so that the strengthening effect is neutralised after quite a short the process is very complicated. The second option has the disadvantage, besides the difficulty of achieving complete coating of the glass, that adhesion of the coated glass to the concrete matrix is poor. The third option does not avoid corrosion of the glass, but only delays it. In addition, there is also the disadvantage of poorer adhesion. The fourth option has the disadvantage that the fibres have to be drawn at relatively high temperatures.

An object of the present invention is to produce glass which does not have the disadvantages referred to above. This object is achieved according to the invention with glass in which cations are present which produce reaction products with the cement on the fibre surface, which products protect the glass from further corrosion and strengthen the effect of the zinc.

It is known that zinc oxide delays the age-hardening of Portland cement and increases the heat of reaction of the age-hardening process. Heat is released during age-hardening and thus, by measuring the thermal effect, a selection procedure can be adopted to determine those oxides which are suitable for solving the task of the present invention.

The procedure was applied to a plurality of oxides. It was found that there are several metals which qualitatively react similarly to

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Page 1, Heading, (72), Inventor, *for* COEMEN *read* COENEN

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This invention relates to glass compositions and is concerned with glass which, in the form of fibres, is suitable as a reinforcement for cement, mortar and concrete or which, in the form of hollow spheres or in aerated form, is suitable for incorporation in light concrete.

It is known that the resistance of cement, mortar and concrete to stress, impact and abrasion can be considerably increased by the addition of glass fibres. The use of hollow glass spheres or glass in aerated form, i.e. aero glass, as an aggregate in light concrete has the advantage of increasing the resistance to pressure and of an absence of water absorption as compared with polystyrene or other aerated plastics. In Portland cement, however, fibres or hollow spheres of the usual types of glass are rapidly corroded because of the high pH, so that the strengthening effect is neutralised after quite a short time.

Various measures have been suggested to prevent this corrosion, for example:—

1) lowering the pH value by the use of carbon dioxide in preparing the concrete or by introducing carbon dioxide into solid concrete;
2) coating the glass fibres with alkali-resistant plastics materials;
3) using fibres or spheres made of highly alkali-resistant glass;
4) using fibres made of alkali-free types of glass containing zinc (see German Patent Specification No. 2,129,016).

The first option has the disadvantage either that the glass can only be inserted in porous concrete, or that for solid concrete the process is very complicated. The second option has the disadvantage, besides the difficulty of achieving complete coating of the glass, that adhesion of the coated glass to the concrete matrix is poor. The third option does not avoid corrosion of the glass, but only delays it. In addition, there is also the disadvantage of poorer adhesion. The fourth option has the disadvantage that the fibres have to be drawn at relatively high temperatures.

An object of the present invention is to produce glass which does not have the disadvantages referred to above. This object is achieved according to the invention with glass in which cations are present which produce reaction products with the cement on the fibre surface, which products protect the glass from further corrosion and strengthen the effect of the zinc.

It is known that zinc oxide delays the age-hardening of Portland cement and increases the heat of reaction of the age-hardening process. Heat is released during age-hardening and thus, by measuring the thermal effect, a selection procedure can be adopted to determine those oxides which are suitable for solving the task of the present invention.

The procedure was applied to a plurality of oxides. It was found that there are several metals which qualitatively react similarly to zinc, but which do not act so intensively. Another type of oxide counteracts delay, whilst a third causes a lesser thermal effect.

Glass for use in reinforcing concrete includes, according to the invention, oxides of zinc and selected metals which delay age-hardening and increase the thermal effect or at least do not reduce it. On the other hand, those metal oxides which affect the delay negatively, or reduce the size of the thermal effect should not be present in the glass, or only in harmless concentrations. The term 'metal oxide' as used herein includes oxides of silicon, arsenic, antimony and boron.

The oxides which have been tested fall into four groups, as follows:—

1) those with a positive action:
ZnO, CuO, TiO_2, Fe_2O_3,
2) those which are neutral:
SiO_2, ZrO_2, SrO, BaO, MNO_2, NiO,
3) those with a negative action:
As_2O_5, Sb_2O_5, V_2O_5, B_2O_3, M_2O (M=alkali metal), PbO, CdO, SnO_2, and
4) a special section:
Al_2O_3, MgO, CaO.

The oxides of the "special section" can act positively or negatively dependent on the concentrations of other oxides in the glass. Thus, for example, the effect of the oxides classified under "positive" is neutralised if the molar ratio of, for example, $CaO:ZnO$ is greater than 0.5:1.

According to the invention there is provided glass consisting of SiO_2, ZnO and one or more of TiO_2, CuO, Fe_2O_3, BaO, CaO, MgO aid Al_2O_3, wherein the percentages by weight of the constituents of the glass are as follows:—

SiO_2	20 to 70,
ZnO	5 to 70,
TiO_2	0 to 20,
CuO	0 to 10,
Fe_2O_3	0 to 15,
BaO	0 to 30,
CaO	0 to 10,
MgO	0 to 15,
and	
Al_2O_3	0 to 30,

the concentrations of the glass constituents further being such that the ratio of the molar total of Al_2O_3, MgO and CaO, if present, to the molar total of ZnO, CuO, TiO_2 and Fe_2O_3 is less than or equal to 0.5:1.

The glass preferably contains at least one of Al_2O_3, TiO_2 and CuO in the following percentages by weight:—

Al_2O_3	10 to 30,
TiO_2	3 to 12,
and	
CuO	0.2 to 5.

The invention will now be illustrated with reference to the following example:

Glass of the composition (in weight %) 44.5 SiO_2, 51.0 ZnO and 4.5 CuO was melted in a crucible in a gas furnace with 1% $BaSO_4$ added as a refining agent. The glass was partly drawn out of the crucible in an upwards direction to form fibres of about 30 μm diameter. The remainder of the glass was poured out, quenched and ground to a grit of an average grain size of 10 to 40 μm. The grit was mixed with 30% Portland cement P 375 and the mixture had water added to it corresponding to a water value of 0.35. The mixture was put into a beaker and the temperature thereof was measured with a thermocouple element and plotted as a function of time. A delay in temperature increase occurred in relation to pure cement with an increase in the thermal effect.

The fibres different from normal glass fibres by having a very low coefficient of relative sliding friction, this being caused by the presence of copper oxide in the glass. The fibres were suspended in concentrated grout in a polyethylene bottle. From time to time fibres were removed and tested for tensile strength. The tensile strength decreased in the first two days by 20% of its initial value, but then remained constant over a period of several months relative to the tensile strength of the neutral fibres.

WHAT WE CLAIM IS:—

1. Glass consisting of SiO_2, ZnO and one or more of TiO_2, CuO, Fe_2O_3, BaO, CaO, MgO and Al_2O_3, wherein the precentages by weight of the constituents of the glass are as follows:—

SiO_2	20 to 70,
ZnO	5 to 70,
TiO_2	0 to 20,
CuO	0 to 10,
Fe_2O_3	0 to 15,
BaO	0 to 30,
CaO	0 to 10,
MgO	0 to 15,
and	
Al_2O_3	0 to 30,

the concentrations of the glass constituents further being such that the ratio of the molar total of Al_2O_3, MgO and CaO, if present, to the molar total of ZnO, CuO, TiO_2 and Fe_2O_3 is less than or equal to 0.5:1.

2. Glass according to claim 1, containing between 10 and 30% by weight Al_2O_3.

3. Glass according to claim 1 or 2, containing between 3 and 12% by weight TiO_2.

4. Glass according to any preceding claim, containing between 0.2 and 5% by weight CuO.

5. Glass according to any preceding claim, drawn into fibres.

6. Glass according to any of claims 1 to 4, blown into hollow spheres or manufactured as aerated glass.

7. Glass having a composition substantially as hereinbefore described with reference to the Example.

8. A method of reinforcing concrete which includes the use of glass according to any one of the preceding claims.

9. Reinforced concrete, the reinforcement of which consists of glass according to any one of claims 1 to 7.

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